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An Aromatic Schiff Base Stabilised As a Coordinated Enol Iminium Zwitterion by Complex Formation with a Series of Divalent Metal Ions

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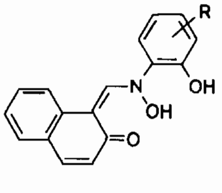
Abstract

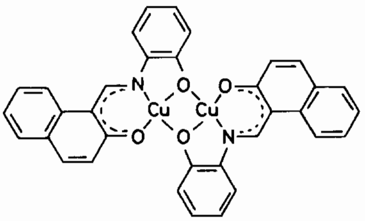
The Schiff base N-(2-hydroxy-3-carboxy-1-naphthylidine)-4-methyl-2-sulphonic acid aniline (bonsa-H_3) has been found to react with a range of divalent metal ions (Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) and $UO_2{}^{2+}$ to give red-yellow insoluble complexes (bonsa-$H)_m(H_2O)_n$. The solid state diffuse reflectance spectra of all the complexes have an intense visible band at *ca.* 470 nm. This fact, together with evidence from infrared spectra and room-temperature magnetic-moment measurements, suggests that in all cases the ligand is coordinated to the metal ion in the solid state in the enol-iminium zwitterionic form. The ^1H NMR spectra of the Mg^{2+} and Zn^{2+} complexes in DMSO-d_6 indicate that a different structure is adopted in this solvent. Comparisons with the spectra of bonsa-H_3 and (bonsa-H_2)K·H_2O suggest that the solution structure is that of an enol-imine.

Introduction

Although Schiff-base metal complexes have received extensive investigation [1], the spectroscopic and structural properties of 2-hydroxy-1-naphthaldehyde derivatives are less well studied. The Schiff bases derived from 2-hydroxy-1-naphthaldehyde and *o*-hydroxy aromatic amines have been shown [2] to exist as *β*-keto amines (Fig. 1) and form neutral, planar complexes with divalent metal ions [3]. The Cu(II) derivative, II, has a dimeric structure [4].

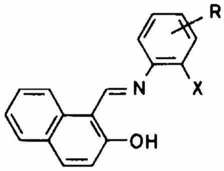


I



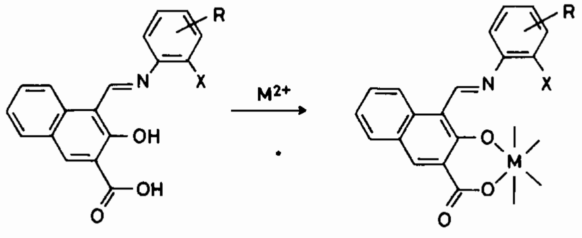
II

The use of aromatic amines with ortho substituents other than -OH (or similar donors such as -SH, -NH_2) leads to Schiff bases, III, which are unable to accommodate a metal ion unless there is a considerable distortion from a planar configuration [5, 6]. However, the provision of an alternative metal-ion site by the use of precursor aldehydes such as 2-hydroxy-3-carboxy-1-naphthaldehyde [7] will allow for the coordination of a metal ion to give a 1:1 complex without distortion of the planar [8] Schiff base (IV–V). It is to be expected, however, that the stability of complexes such as V will be strongly dependent on the nature of M^{2+} and the size and/or electronic properties of X and R.



X = H, CH_3, CO_2H, etc.

III



IV V

If X or R is an acid group, a modification of V is made possible by protonation of the basic azomethine nitrogen atom, leading to the formation of a zwitterionic complex such as VI. In this type of complex, the coordinated Schiff base is in the favoured enol-iminium form. It seems reasonable to suppose, therefore, that a complex of type VI will be more likely to retain its structure than one of type V, where a small distortion might favour metal–nitrogen coordination.

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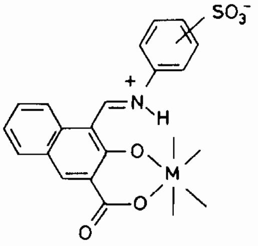
The structures of the azomethine–metal complex, II, and the proposed complexes of types V and VI will be important in determining their respective colours. This fact is of consequence in view of the interest in azomethine complexes as pigments [9]. In metal derivatives related to II, for example, it has been suggested that some intense bands in their visible spectra are due to 'metal–nitrogen' charge-transfer transitions [10]. In complexes of type V and VI, the metal ion is likely to be less directly involved in the chromophore and this could offer greater flexibility in the design and synthesis of metal-containing pigments.



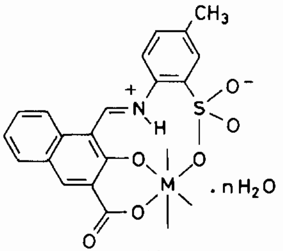
VI

Previous workers [11] have shown that the principal long-wavelength visible absorption bands of the various forms of *o*-hydroxy aromatic azomethines are, in order of increasing energy: zwitterion; anion ≃ cation; enol. The colours of complexes of type VI are, therefore, expected to be deeper than those of type V. This fact, together with the expected advantage of greater stability, makes the type VI series more attractive as a subject of study.

We have prepared some complexes of type VI and obtained their solid-state diffuse reflectance visible spectra and infrared spectra in an attempt to establish their solid-state structures. Magnetic moments of some of the complexes have also been measured. In addition, NMR and infrared studies in solution have been undertaken in order to assess the stabilities of the complexes and to determine their structures in a polar solvent.

Results and Discussion

Complexes of type VI were successfully prepared using an *ortho*-sulphonic acid amine as the Schiff-base precursor. This isomer was chosen so that the bulky sulphonate might provide an effective 'block' to metal–nitrogen coordination and be more likely to cause the metal ion to complex with the oxygen coordinating groups. In addition, it presents a possibility for intra-molecular H-bonding involving the azomethine hydrogen atom. The divalent metal ions Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} all formed hydrated 1:1 complexes corresponding to the formula VII, for which satisfactory analyses were obtained (Table I).



VII

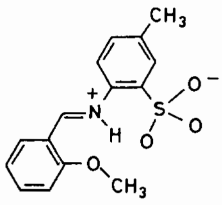
All the isolated derivatives are bright red-yellow in colour and all possess an intense band at about 470 nm in their solid-state diffuse reflectance spectra. This would appear to indicate that each of the complexes has a similar chromophore and that this is effectively independent of the metal ion. The posi-

TABLE I. Elemental Analyses of the Compounds Prepared.

Compound	Carbon %		Hydrogen %		Nitrogen %	
	Calc.	Found	Calc.	Found	Calc.	Found
(bonsa-H)Mg$(H_2O)_6$	44.27	44.62	4.84	4.24	2.71	2.94
(bonsa-H)Mn$(H_2O)_{1/2}$	57.43	57.36	3.02	3.40	3.52	2.96
(bonsa-H)Co$(H_2O)_{3\frac{1}{2}}$	45.32	45.40	3.97	4.20	2.78	2.96
(bonsa-H)Ni$(H_2O)_5$	43.02	43.14	4.34	4.05	2.64	2.62
(bonsa-H)Cu$(H_2O)_{2\frac{1}{2}}$	46.53	46.25	3.67	3.63	2.86	2.80
(bonsa-H)Zn$(H_2O)_2$	47.11	46.93	3.51	4.08	2.89	2.63
(bonsa-H)$UO_2(H_2O)_{2\frac{1}{2}}$	32.66	32.61	2.57	2.38	2.01	1.94
(bonsa-H_2)K(H_2O)	51.70	51.31	3.63	3.35	3.17	2.76
(bonsa-H_3)	59.22	60.16	3.89	4.01	3.63	3.27
N-(2-methoxybenzylidine)-4-methyl-2-sulphonic acid aniline	59.02	59.52	4.91	5.06	4.59	4.43

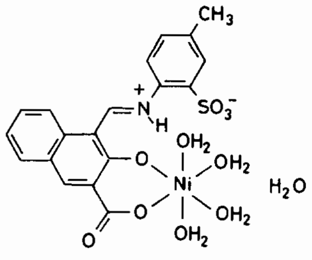
tion of the absorption band suggests that the coordinated Schiff base is present in the enol-iminium zwitterionic form [12], as in the proposed structure VII.

The infrared spectra (Nujol mulls) of the complex are also similar. Minor differences occur in the 1150–1250 cm^{-1} region, which is associated with vibrations of the -SO_3^- group but in no cases are there bands attributable to free carboxylic acid or free sulphonic acid groups [13]. In the region 3650–2800 cm^{-1} in which an ν(N–H) band might be expected to occur, a broad band present in all the spectra is probably mainly due to coordinated water [14] which may obscure ν(N–H). In this connection, the anhydrous Schiff base VIII shows a medium-intensity band at 3505 cm^{-1} which can be assigned to a ν(N–H) [15] and no bands which might be attributed to a free sulphonic acid group.



VIII

Room-temperature magnetic-moment measurements on the nickel and cobalt complexes (VII: M = Ni, n = 5, M = Co, n = 3½) indicate only a small contribution from orbital angular momentum. The divalent ions possibly have a low-symmetry six-coordinate geometry. The conclusion, therefore, is that in these and all the other metal derivatives, the metal ion is coordinated to the carboxylic and naphtholic oxygen atoms and that in the solid state, the remaining coordination positions are occupied by water molecules (*e.g.*, IX). Although there is no direct evidence for coordination of the metal ion to the naphtholic oxygen atom, it seems reasonable in view of the known chelating ability of salicylic acid [16].



IX

The visible spectrum of each of the complexes in solution (methanol, 10 mg per litre) reveals the principal band to be at a shorter wavelength than in the solid state (Table II). Furthermore, in the solid-state diffuse reflectance spectrum, this band occurs at *ca.* 470 nm for the Mg^{2+}, Mn^{2+}, Ni^{2+} and UO_2^{2+} derivatives, at *ca.* 435 nm for the Co^{2+} and Zn^{2+} and at 404 nm for the Cu^{2+} derivative. While it is impossible to draw firm conclusions from these observations, it seems likely that the proposed solid-state structure, VIII, is not retained by any of the derivatives in methanol solution.

An infrared spectrum of (bonsa-H)$Zn(H_2O)_2$ in DMSO solution shows a number of changes from that in the mull. In the 1630–1730 cm^{-1} region, two new bands appear at 1650 and 1700 cm^{-1}. The latter, which is of medium intensity, strongly suggests the presence of a carboxylic acid group. It is probable, therefore, that in the case of at least one complex there are important differences in structure between the solid and the dissolved species.

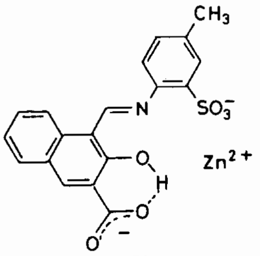
In order to understand better the behaviour of the complexes in solution, an examination of the ^1H NMR spectra of (bonsa-H)$Mg(H_2O)_6$ and (bonsa-H)$Zn(H_2O)_2$ in DMSO-d_6 was undertaken.

The spectrum of a freshly prepared solution of the zinc complex in DMSO-d_6 shows a broad, concentration-independent singlet absorption at 15.8 δ (TMS = 0.0 δ) corresponding to one proton. The extremely low-field position of this resonance indicates strong hydrogen bonding [17] and the peak is therefore

TABLE II. Principal Long-Wavelength Absorption in the Electronic Spectra of the Complexes (nm).

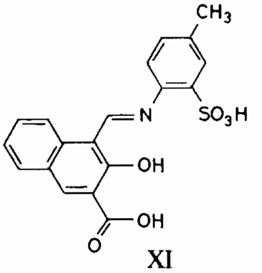
Complex	MeOH solution (10 mg per litre)	Solid state diffuse reflectance
(bonsa-H)$Mg(H_2O)_6$	452	470
(bonsa-H)$Mn(H_2O)_{1/2}$	450	470
(bonsa-H)$Co(H_2O)_{3\frac{1}{2}}$	434	472
(bonsa-H)$Ni(H_2O)_5$	456	474
(bonsa-H)$Cu(H_2O)_{2\frac{1}{2}}$	404	472, 490sh
(bonsa-H)$Zn(H_2O)_2$	436	470, 486sh
(bonsa-H)$UO_2(H_2O)_{2\frac{1}{2}}$	452, 470sh	468, 492sh

assigned to an intramolecularly bonded hydroxyl/acid [18] proton. The structure of the zinc complex in DMSO solution is then assumed to be that of an enol-imine, with the metal ion probably associated with the carboxylate group as in X. This structure is consistent with the solution infrared spectrum previously discussed, if it is assumed that the H-bonded proton is shared between the naphthol and carboxylic acid groups. On the NMR time-scale, the two sites would not be distinguishable. The analogous magnesium complex has an almost identical ^1H NMR spectrum in DMSO-d_6, except that in this case the low-field singlet absorption is at 16.9 δ (1H) and is sharper than in the zinc derivative. This difference probably reflects the influence of the metal ion in the hydrogen bond but the ^1H NMR spectra suggest that the magnesium complex has essentially the same structure as the zinc analogue in freshly prepared DMSO solutions. On allowing either solution to stand for some hours, the low-field peak is replaced by one at 10.6 δ (the same position in both complexes). This new resonance we assign to a hydroxyl proton which is hydrogen-bonded to a molecule of solvent.



X

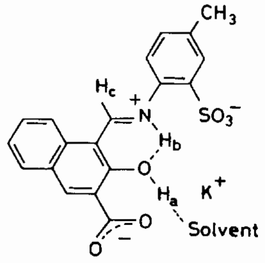
Further evidence in support of the above assignments and of the postulated solution structure, X, is provided by an examination of the ^1H NMR spectra of the free ligand, bonsa-H_3, and its monopotassium salt.



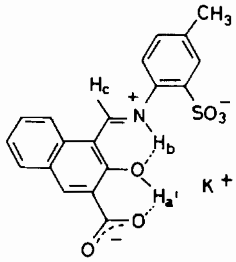
XI

The spectrum of bonsa-H_3 in DMSO-d_6 down field of 10 δ shows just one sharp singlet peak at 10.7 δ. This is assigned to the hydroxyl proton which is hydrogen-bonded to a solvent molecule, a resonance identified in the metal-complex spectra. A broad absorption at 8.5 δ is assigned to the combined resonances of the acid group protons and those of the water of hydration which are undergoing exchange.

The ^1H NMR spectrum* of (bonsa-H_2)K·H_2O in DMSO-d_6 shows three resonances down-field from 10 δ. The singlet at 10.64 δ, by analogy with a similar peak in the spectra of the ligand and zinc and magnesium derivatives, is assigned to the hydroxyl proton H_a (see diagram XII) which is hydrogen-bonded to a solvent molecule. A doublet centred at 14.60 δ is assigned to the azomethine proton H_b which is coupled to the hydrogen atom H_c on the adjacent carbon [19]. The low-field position of the H_b resonance signal suggests strong intramolecular hydrogen bonding. The doublet due to the H_c resonance is located at 9.4 δ and J_{bc} = 13.7 Hz. The magnitude of J is within the range expected for coupling between protons '*trans*' to one another across a double bond [17].



XIIa



XIIb

The third low-field resonance in the ^1H NMR spectrum of (bonsa-H_2)K·H_2O is a broad singlet at 16.24 δ. Again by analogy with the zinc and magnesium complexes, whose freshly prepared solutions show a resonance peak in this region, we assign this singlet to an intramolecularly hydrogen-bonded hydroxyl proton Ha' as in XIIb. The three low-field resonances of the mono-potassium salt together integrate to two protons and the doublet to one. Solutions of this salt in DMSO are therefore postulated to contain both species XIIa and XIIb.

The solid-state diffuse reflectance spectrum of (bonsa-H_2)K·H_2O has its principal visible band at 463 nm. The band is in the same position in DMSO solution (464 nm, ϵ 16,000) and this suggests that, unlike the divalent-metal derivatives, (bonsa-H_2)K·H_2O has a similar structure in the solid state and in solution. The infrared spectrum of the monopotassium salt (Nujol mull) has a medium-intensity band at 1700 cm^{-1} which probably indicates the presence of a carboxylic acid group. This is consistent with the solution structure XIIb, in which the proton Ha' is shared between the naphtholic and carboxylic oxygen atoms. The 1700 cm^{-1} infrared band would also seem to correspond to a similar band, in the same position, in the spectrum of (bonsa-H)Zn$(H_2O)_2$ in DMSO. This further supports the view, arrived at on the basis of ^1H NMR studies, that the zinc complex has the structure of an enol-imine, X, in this solvent.

Experimental

Physical Measurements

Visible spectra in solution and in the solid state (diffuse reflectance) were recorded on a Pye-Unicam SP1800. A Perkin-Elmer 457 was used to record the infrared spectra, which were calibrated with polystyrene. ^{1}H NMR spectra were recorded on Perkin-Elmer R14 and JEOL-PS-100–PFT100 spectrometers at 100 MHz. TMS was used as the internal reference. Magnetic susceptibilities were measured by the Gouy method.

Preparations

The metal complexes (bonsa-H)M(H_2O)$_n$ were prepared using the same general method. This is illustrated here by the preparation of [(bonsa-H)Cu(H_2O)$_2$]$_2$.

[(bonsa-H)Cu(H_2O)$_2$]$_2$

2-hydroxy-3-carboxy-1-naphthaldehyde (0.216 g, 0.001 mol) dissolved in warm ethanol (20 cm^3) was added to a solution of 4-methyl-2-sulphonic acid aniline (0.19 g, 0.001 mol) in hot water (20 cm^3). The resulting orange solution was cooled and filtered. Copper acetate (0.2 g, 0.001 mol) dissolved in water (10 cm^3) was then added dropwise while the orange solution was stirred. A yellow precipitate developed and, after stirring for a further 15 minutes following addition of all the metal acetate, this was filtered off, washed with water and dried over silica gel under vacuum. The yield of [(bonsa-H)Cu(H_2O)$_2$]$_2$ was 0.37 g, 75%. Yields in the preparations of the other divalent-metal derivatives by the same method were in the range 70–80%.

(bonsa-H_2)K·H_2O

4-methyl-2-sulphonic acid aniline (0.44 g, 0.0024 mol) was dissolved in a solution of potassium hydroxide (0.27 g, 0.0048 mol) in water (10 cm^3). The solution was filtered and then heated on a steam bath. A solution of 2-hydroxy-3-carboxyl-1-naphthaldehyde (0.51 g, 0.0024 mol) in hot ethanol (10 cm^3) was then added. On cooling the solution to room temperature, orange crystals of the salt began to form. After standing overnight, the crystals were filtered off, washed with water and dried over silica gel under vacuum. Yield = 0.232 g, 22%.

bonsa-H_3

2-hydroxy-3-carboxy-1-naphthaldehyde (0.216 g, 0.001 mol) dissolved in ethanol (10 cm^3) was added to a solution of 4-methyl-2-sulphonic acid aniline (0.187 g, 0.001 mol) in hot water (20 cm^3). The solution was boiled on a steam bath and its volume reduced until a precipitate began to form. After cooling to room temperature and standing for some hours, the yellow solid was filtered off. The somewhat unsatisfactory analysis result for carbon reflects the difficulty in isolating this water-soluble material without causing a certain amount of decomposition. However, it is felt that the figures (see Table I) are good enough to support the formula XI and can be tolerated, since the compound is used only as an aid in NMR assignments.

N-(2-methoxybenzylidine)-4-methyl-2-sulphonic Acid Aniline

4-methyl-2-sulphonic acid aniline (0.74 g, 0.004 mol) was dissolved in boiling water (30 cm^3). The boiling solution was stirred and to it was added, dropwise, a solution of *o*-methoxybenzaldehyde (0.544 g, 0.004 mol) in ethanol (5 cm^3). Yellow silky needles of the Schiff base immediately precipitated and stirring was continued at 60 °C for a further 30 mins. The reaction mixture was then cooled to room temperature and the solid was filtered off, washed with water and a little ethanol and dried over silica gel under vacuum. Yield = 0.99 g, 81%.

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